

All the adiabatic bound states of NO₂ (J=0)

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Abstract

We calculated all 2967 even and odd bound states of the adiabatic ground state of NO₂, using a modification of the *ab initio* potential energy surface of Leonardi et al. [J. Chem. Phys. **105**, 9051 (1996)]. The calculation was performed by harmonic inversion of the Chebyshev correlation function generated by a DVR Hamiltonian in Radau coordinates. The relative error for the computed eigenenergies (measured from the potential minimum), is 10⁻⁴ or better, corresponding to an absolute error of less than about 2.5 cm⁻¹. Near the dissociation threshold the average density of states is about 0.2/cm⁻¹. Statistical analysis of the states shows some interesting structure of the rigidity parameter Δ_3 as a function of energy.

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I. INTRODUCTION

The complexity of the spectrum of NO_2 has always been a challenge, both to experimentalists and theorists. Well-resolved spectra were first measured only after the advent of the laser, and the introduction of cooled molecular beams allowed the measurement of *complete* spectra in certain energy ranges (still not up to the dissociation limit) [1–4]. One reason for the spectral congestion is the conical intersection (found by Gillespie *et al.* in 1975 [5]) mixing the \tilde{X}^2A_1 electronic ground state surface at an energy of only 1.289 eV with the first excited \tilde{A}^2B_2 surface. The dissociation energy V_{diss} of \tilde{X}^2A_1 is 3.226 eV. In the experiment, this leads to disturbed progressions and increased state density, while the theorist is forced to include the vibronic coupling in the calculation of more than the lowest few vibrational states of the molecule [6,7].

There are only a few molecules for which anything like a full list of vibrational states (even for $J = 0$) has been calculated. Examples are the pioneering work of Tennyson *et al.* [8] on H_3^+ , and the more recent calculations on HO_2 [9], HCN [10], H_3^+ [11] and NO_2 [12]. The reason for this situation is, of course, the immense computational expense of such calculations, which one generally applies only to potential energy surfaces (PES) which are quite well known. These, however, are still scarce.

In this paper we present first results of an effort to compute bound and resonance states of NO_2 . Two developments were of great help to us: first the calculation of good PESs for the two lowest electronic states of NO_2 including their coupling by the Siena-Wuppertal group [12]; second, the advent of the filter diagonalization method [13–17] for solving large eigenvalue problems. The first step of this endeavour, which we report here, is the calculation of all (~ 3000) adiabatic bound states of the ground PES. This in itself is non-trivial, since near the dissociation limit the average state density is ~ 0.2 states per cm^{-1} for each of the two symmetry species. The computation of non-adiabatic energy eigenvalues, which includes the surface coupling, is under way [18], and the method itself allows the introduction of imaginary absorption potentials, and, therefore, the extension of the calculations to resonances. (This

has been tested for H_3^+ [17])

Another benefit of this project is the possibility to perform a thorough statistical analysis over the whole energy range of a molecular system. This has so far been almost impossible for real molecules, because of missing data in the experiments, or an insufficient number of eigenstates in the calculation, both leading to large statistical errors [3,4,6,7].

In the following we discuss first some properties and necessary modifications to the PES of ref. [12], then the computation, and, finally, some results on the statistics of the computed levels.

II. THE POTENTIAL ENERGY SURFACES

Since the two lowest adiabatic PESs of NO_2 have a conical intersection at an energy of about one third of the dissociation energy, they must both be considered in any calculation of more than the lowest few vibrational states [6]. However, the intersection makes their direct interpolation impractical. Instead, one interpolates the diabatic surfaces V_{11} and V_{22} , and, in addition, their coupling V_{12} . From such fits one computes the energies of the two adiabatic surfaces V_X (ground state) and V_A (first excited state) whenever they are needed from

$$V_{X/A}^{\text{adiab}} = \frac{1}{2}(V_{11} + V_{22}) \mp \sqrt{\frac{1}{4}(V_{11} - V_{22})^2 + V_{12}^2} \quad (1)$$

The surfaces used in our calculations have been derived in several steps from nearly 1000 *ab initio* points computed in ref. [19]. These points have been diabaticized [20,19] by a unitary transform, demanding that certain dipole matrix elements be small. All computed points are in the region (here we use bond coordinates) $2.08a_0 \leq r_1, r_2 \leq 2.50a_0$, $70^\circ \leq \beta \leq 180^\circ$, called region D in ref. [20]. To produce surfaces useful for the calculation of vibrational levels, they had to be fitted to an analytical form, furthermore they had to be extrapolated to regions outside of region D, i.e. to shorter and larger interatomic distances, and to small angles. This has been done in several iterations by the Siena and Wuppertal groups [19,21,12], who

also utilized empirical data from the measured NO₂ spectrum (see ref.[1] in [12]) to improve the final fits of ref. [12]. It is these fits, called here V_{ik}^{LP} (for Leonardi-Petrongolo) from which we started.

While the authors of ref. [12] had no problems to compute vibrational energies with their fits, early test calculations with our method showed that the short- and long-range extrapolations in V_{ik}^{LP} have (unphysical) kinks, which cannot be tolerated when a discrete variable representation (DVR) is used. Therefore, we modified the surfaces by smoothing out the kinks as described below. Preliminary calculations done by C. Petrongolo [22] with this surface using the code from ref. [12], and our nonadiabatic computation [18] show an equally good agreement with experimental data at energies up to 1.22 eV. Additionally, our surface modification improves the computed state density up to 2.3 eV, which had been too high compared with the experimental one in ref. [12].

In detail, the following modifications were applied (energies are hartree units = 27.211396 eV, distances bohr units $a_0 = 0.529177 \cdot 10^{-10}$ m):

(a) The short-range correction (for $r_i < 2.08$) of the lower diabatic surface V_{11}^{LP} was changed to (shown only for r_1 , but similar for r_2):

$$\begin{aligned} V_{11}(r_1, r_2, \beta) &= V_{11}^{LP}(r_1, r_2, \beta)(1 - Q(a, br_1)) \\ &+ (6.00(r_1 - 2.08)^2 - V_{11}^{LP}(2.08, r_2, \beta))Q(a, br_1) \\ V_{11}^{LP} &\in D, \end{aligned} \tag{2}$$

here the function $Q(a, br) = 1 - P(a, br)$ is the incomplete gamma function cf. ref. [23]) and the parameters a and b are listed in Table I.

(b) The short-range correction to V_{22} was dropped, and $V_{22}(r_1, r_2, \beta)$ set to a finite high value $V_{22}(1.50, r_2, \beta)$ for $r_1 \leq 1.50$, and similarly for $r_2 \leq 1.50$.

(c) The small angle ($\beta < 70^\circ$) corrections to the potentials V_{11} and V_{22} were dropped completely.

(d) For small and large angles ($\beta < 70^\circ$ and $\beta > 131^\circ$) the coupling potential was smoothly set to zero:

$$V_{12}(\beta) = V_{12}^{LP}(\beta)(1 - Q(a, b(\beta - 71^\circ))) \text{ for } \beta < 71^\circ \quad (3)$$

$$V_{12}(\beta) = V_{12}^{LP}(\beta)(1 - Q(a, b(\beta - 131^\circ))) \text{ for } \beta > 131^\circ. \quad (4)$$

The values used for the parameters a and b are listed in Table I.

(e) The long-range correction of the diagonal potentials V_{ii} , which are necessary to produce the correct dissociation limits, were modified by changing the switching function, now reading (for $r_1 > r_{\max} = 3.00$)

$$V_{ii}(r_1, r_2) = (1 - Q(1, b(r_1 - r_{\max})))V_{ii}^{LP} + Q(1, b(r_1 - r_{\max}))(V_{\text{diss}} + V_{\text{NO}}(r_2)). \quad (5)$$

and similar for r_2 . The parameters a and b are again listed in table I.

III. COMPUTATION

For computing bound states of NO_2 we use the low-storage version of the filter-diagonalization method introduced recently by Mandelshtam and Taylor [16]. This method is conceptually based on the filter-diagonalization procedure of Wall and Neuhauser [14] which extracts the system eigenenergies by harmonic inversion of a time correlation function $C(t)$. The method of ref. [16] is designed for a direct harmonic inversion of the Chebyshev correlation function [24]

$$c_n = \langle \xi_0 | T_n(\hat{H}) | \xi_0 \rangle \sim \sum_k d_k \cos n\omega_k, \quad (6)$$

for the eigenenergies $E_k = \cos \omega_k$ and amplitudes d_k . The computation of the c_n sequence is done to essentially the machine precision using a very inexpensive iterative numerical scheme,

$$\xi_1 = \hat{H}\xi_0, \quad \xi_{n+1} = 2\hat{H}\xi_n - \xi_{n-1}, \quad (7)$$

with c_n being generated using $c_{2n} = 2\langle \xi_n | \xi_n \rangle - c_0$, $c_{2n-1} = 2\langle \xi_{n-1} | \xi_n \rangle - c_1$. This requires to store only a few vectors at a time, assuming that the matrix-vector multiplication is

implemented without explicit storage of the Hamiltonian matrix. The spectral analysis part (i.e., the harmonic inversion of c_n by the filter-diagonalization) is carried out independently and computationally very efficiently after the sequence c_n is computed. All these features assure the very high performance of the overall numerical procedure.

For the Hamiltonian matrix representation we choose Radau coordinates (R_1, R_2, Θ) in which all mixed derivatives in the kinetic energy vanish [25], to account for the C_{2v} symmetry of the NO_2 molecule. The fast application of the Hamiltonian matrix to a vector is achieved by implementing a potential adapted DVR, which we set up in a way which allowed us to identify a single parameter, the potential cutoff energy V_{cut} , on which all other grid parameters depend. The bases for the radial parts of the Hamiltonian are sinc-DVRs [26], characterized by their spatial extensions $R_{i\min}$ to $R_{i\max}$ ($i = 1, 2$), and sizes $n_1 = n_2$, which are diagonalized and then truncated by an energy cutoff to $n_{1b} = n_{2b}$. For the angular part we use a Legendre-DVR [27] characterized by its size n_3 . The angular extension is always 0° to 180° .

Convergence studies in which all grid parameters are varied independently are prohibited in this study by the computing times involved. Instead, these parameters were fixed in 1D calculations, but in a consistent way: We first set an accuracy goal, in this case a relative accuracy of 10^{-4} for states just below the true NO_2 dissociation energy of 3.226 eV. With this desired accuracy we adjust (in 1D calculations at the equilibrium angle Θ_0) the spatial extensions $R_{i\min}$ to $R_{i\max}$ ($i = 1, 2$) of the radial grids, while the sizes n_i are kept very large. Then the sizes of the spatial grids, $n_1 = n_2$, are adjusted to yield this same desired accuracy, similarly for the angular grid (at $R_1 = R_2 = R_0$), whose extension, 0° to 180° , is kept. The equidistant grid spacings of the 1D-DVR points $\Delta R, \Delta \Theta$, on the other hand, determine a maximum kinetic energy,

$$T_{\max}^{\text{radial}} = \frac{\pi^2}{2\mu(\Delta R_0)^2} \text{ and} \quad (8)$$

$$T_{\max}^{\text{angular}} \simeq \frac{\pi^2}{2\mu} \left(\frac{1}{R_1^2} + \frac{1}{R_2^2} \right) \frac{1}{\Delta \Theta^2}. \quad (9)$$

(We used $R_1 = R_0$ and $R_2 = \infty$ as an estimate for the moment of inertia in eq. 9, which

seems reasonable for an almost dissociating wavepacket.)

The larger one of these kinetic energies, which in our example (10^{-4} relative accuracy at 3.226 eV) are 4.5 eV for the radial grids and 8.0 eV for the angular grid, is then used to fix the potential cutoff V_{cut} . For consistency, the radial grids are increased in size such that $T_{\max}^{\text{radial}} = T_{\max}^{\text{angular}}$. Then all DVR-points for which $V(R_1, R_2, \Theta) > V_{cut}$ are deleted. As a final result for the accuracy goal mentioned above we get a primitive grid of $n_1 = n_2 = 127$, $R_{1\min} = R_{1\max} = 1.5a_0$, $R_{1\max} = R_{2\max} = 5.5a_0$, $n_3 = 275$, a 1D truncation of the radial grids to $n_{1b} = n_{2b} = 100$, and a final truncated grid of 1 112 707 points.

A further parameter of the method is the number of iterations of the filter diagonalization, eq. 7, which is one half of the number of Chebyshev coefficients c_n . In addition, for the final stage of the calculation the window parameters E_{\min} , E_{\max} , and the number of window basis functions (described in ref. [28]) have to be fixed. This was done such that the extracted eigenenergies were converged to 6 figures with respect to the sequence of coefficients c_n , i.e. two orders of magnitude better than our overall accuracy goal. This led to a number of 300 000 coefficients, whose calculation for the 8 eV set of one symmetry needed about 30 days of CPU-time on an IBM RS6000/59H.

To ensure that our overall accuracy is in the exponential convergence region, and not in some — misleading — small local convergence minimum [29], we ran four different grids consistent with energy cutoffs of 4, 6, 8 and 8.1 eV. The last one has been used in comparison to the last but one to observe numerical noise, and to have an independent set of eigenvalues ensuring that we do not miss any levels. All inconsistencies between the two largest sets have been cleared.

The errors of the computed eigenvalues can be approximately taken as the noisy difference between the calculation with $V_{cut} = 8.0$ eV and the one with $V_{cut} = 8.1$ eV. As Fig. 1 shows, it increases with energy above about 2 eV, and above 3 eV has a plateau of about 10^{-4} eV. This plateau, which is also shown by the differences of the smaller calculations (with $V_{cut} = 4.0$ and 6.0 eV, respectively), is caused by the common limited spatial extension of the radial basis sets, which do not cover the tails of the high energy wavefunctions exceeding

$R_{i\max}$. Due to a smaller density of DVR points in these bases, their plateau starts earlier than that of $V_{cut} = 8.0$ eV. Apart from that, the errors of the smaller calculations lie in the expected order. Results for the odd states are similar. The fact, that all errors lie below the desired precision, proves the convergence of the 3D computation.

IV. STATISTICAL ANALYSIS OF THE ENERGY LEVELS

Our result consists of the energies of 1606 even and 1361 odd levels of NO_2 [30]. (Note that the symmetries of this adiabatic calculation have no physical meaning for the true non-adiabatic molecule with its dominant conical intersection). At energies below $10\,000\text{cm}^{-1}$ they agree with the published list of experimental values [31] to within an average error of 14 cm^{-1} . Since in that energy region the potential fit has been adjusted using the experimental data, this shows the correctness of our calculation in this energy range. Similar agreement exists between our computed data and those computed in ref. [12].

At much higher energies a comparison with experimental data is questionable due to the inaccuracies of the extrapolated PESs, which we had to use, and the adiabatic approximation. However, statistical analyses are meaningful. So, we have performed separate statistical analyses of the 1606 even and 1361 odd levels. One expects a transition from regular to irregular dynamics with rising energy not later than the conical intersection at 1.289 eV. Since only about 75 even and 50 odd states lie below this energy, nearest neighbor histograms trying to show this effect, suffer from insufficient data. Nevertheless, in Fig. 2 the nearest neighbor distributions of the even states are shown for four different energy windows covering all parts of the spectrum. All distributions imply chaotic dynamics by their Wigner type shape, but only the two high energy distributions contain enough data to be really trustworthy. One may, perhaps, wonder why the adiabatic, uncoupled, ground state PES of NO_2 shows "chaos" at such a low energy. However, one should not forget that (a) any anharmonic PES shows chaos gradually increasing with energy, and (b) that the low-lying conical intersection in NO_2 *indirectly* distorts the shape of the *adiabatic* surfaces very much

compared with, e.g., a triple Morse potential. The contribution of the Born-Oppenheimer breakdown, i.e. the *direct* coupling between the surfaces as such, does not change the level statistics too much [18].

The rigidity of the spectrum, $\Delta_3(L)$ seems to be more robust. It is defined as the local mean square deviation of the level staircase $N(E)$ from the best fitting straight line over an energy range $[E_i, E_{i+L}]$ corresponding to L mean level spacings, namely

$$\Delta_3(L) = \min_{(a,b)} \left\{ \frac{1}{L} \int_{E_i}^{E_{i+L}} [N(E) - aE - b]^2 dE \right\}. \quad (10)$$

We have calculated it for lengths L between 2 and 300 levels for the whole spectrum, and for several fractions of it. We have also used various unfolding procedures [32] (and no unfolding at all, which has no effect at energies above 2.3 eV). We find no energy range in which $\Delta_3(L)$ is near $L/15$, the expectation value for random level positions, which one generally correlates with regular classical dynamics. Instead, taking the usual values of L from 2 to 30, we find $\Delta_3(L)$ slightly above the expectation for a Gaussian orthogonal ensemble (GOE), but never higher than twice that value. Interestingly, when we looked for the fluctuations at a much wider scale, taking L between 100 and 300, we found an energy dependent behavior, which, in addition, differed for the even and odd states.

An example is shown in Fig. 3. For $L = 100$, the expected values for random and GOE sequences are 6.67 and 0.46, respectively. Our results lie between 0.5 and 2.5 in different parts of the spectrum. They are robust against a variation of L between 100 and 300, and against random shifts of the energy levels of up to 0.5%, simulating errors in the diagonalization procedure. To demonstrate that Fig. 3 indeed shows the development of the dynamical structure of the states with energy, we show the more conventional way of computing the averaged statistics $\langle \Delta_3(L) \rangle$ in Fig. 4 for two energy ranges: $0 \leq E \leq 1.3\text{eV}$ below the conical intersection, and $2.5 \leq E \leq 2.8\text{eV}$, where the difference between the symmetries is most prominent. The averaged statistics confirms the data of Fig. 3 as representative. Therefore, we are convinced that these changes of the rigidity of the spectrum with energy are a property of the spectrum of NO_2 , or at least of this model of it.

The saturation of the curves in Fig. 4b was explained by Berry [33] in a semiclassical treatment of an integrable and a totally chaotic system. According to this paper, the value of L_{\max} at which saturation takes place is associated with the period of the shortest classical orbit of the system. At this moment, it is unclear to us, why L_{\max} is different for even and odd symmetries.

In conclusion, we have shown that the calculation of all J=0-states of a non-hydride second row molecule having a few thousand states is feasible, and we foresee that the same holds in the presence of a conical intersection, and for low lying resonances. No supercomputer is needed if one is willing to pay the price of some patience.

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FIGURES

FIG. 1. The reciprocal of the median (taken from a window of 100 eigenvalues) of the density of even states $\rho(E)$, and the median of the absolute errors of the energy eigenvalues of the various computations with respect to the largest calculation (with $V_{cut} = 8.1$ eV) *vs.* energy.

FIG. 2. Nearest neighbor distributions of the even states for four different energy ranges: (a) below the conical intersection, (b) about the conical intersection, (c) slightly, and (d) high above the conical intersection. The best fits to Poisson and Wigner distributions are also shown.

FIG. 3. Δ_3 statistics for a window of 100 even (solid line) and odd (dashed line) levels shifted in steps of 10 over the energy range. The Δ_3 value is assigned to the energy in the middle of the window. The horizontal line is the value of the corresponding Δ_3 for a Gaussian orthogonal ensemble (GOE).

FIG. 4. The averaged Δ_3 statistics and its rms error for a window of L states moved between (a) 0 and 1.3 eV, and (b) 2.5 and 2.8 eV. The expectation values for Poisson statistics (P) and the Gaussian orthogonal ensemble (GOE) are also shown.

TABLES

TABLE I. Values of the parameters a and b of the incomplete Gamma function used to switch between potential parts.

correction	a	b [a_0^{-1}]
short-range V_{11}	1.1	-30.0
long-range V_{11}	3.5	6.34902
long-range V_{22}	2.0	2.09979
angle V_{12}	2.0	20.0







